November 30, 1962

Progress Report No. 3
Project 1158-5

Dear Norbert:

This report is a continuation of the work reported June 14 (Progress Report No. 2). As an extension of the early report, we have reduced the film data to tabular form. However, they have not been placed on cards according to the ASTM x-ray diffraction system, because an interest was expressed to reproduce the information, using the Termatrex System. The information for this system has been requested from ASTM and the manufacturer of the equipment, but has not been received as yet. However, the data may be transferred readily to whatever system is desirable.

This report also terminates the first year of work on Project 1158-5, but we are continuing as advised by Lynn and you until the extension comes.

Sufficient funds are available to continue this work for the next 30 to 60 days, at least. The work during this interim shall be along the direction recommended.

Synopsis of Previously Reported Work

In Progress Report No. 2, 14 June 1962, we described the essentials for producing x-ray diffraction patterns from powdered samples. In brief, these are a source of x-rays, a pinhole collimator to produce a very narrow beam of x-rays, a means for holding the sample in the narrow x-ray beam,

Our x-ray source is a General Electric Type CA-7 tube with a copper anode. The tube is operated at about 35 kilovolts peak by a G. E. XRD-5 power supply. The G. E. equipment provides a table for mounting the x-ray tube and the diffraction apparatus. The collimating pinholes, the sample, and the photographic film are all supported in a Philips Micro Camera purchased specifically for this project. The micro diffraction camera is positioned with the collimator very close to the window of the x-ray tube. The camera is aimed very precisely for maximum x-ray intensity with the aid of a fluorescent screen behind the film holder.

The collimator consists of pinholes in two lead discs spaced about one cm apart. The holes are 0.35 mm diameter. The sample is held very close to the collimator in the hole in a brass washer. The brass washers are 0.25 in. diameter by 0.06 in. thick. The average hole used was about 0.5 mm diameter by 0.5 mm long.

The film is about the size of a postage stamp and is held about 1.5 cm from the sample. We use mainly Ilford Type G industrial x-ray film.

Figure 3 of this report consists of representative diffraction patterns. The diffraction patterns are interpreted using Bragg's equation.[1,2]

$$n\lambda = 2d \sin \theta$$

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[1] Clark, G. L., Applied X-Rays, McGraw-Hill, New York, 1955, pp. 95 - 102.
[2] Azaroff, L. V., Norelco Reporter, Vol. VI, Nos. 4 - 5, pp. 76 - 79.

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where n is the order of diffraction (always an integer), λ is the wavelength of
x-rays used (1.54 Angstrom units), d is the spacing of the atomic planes con-
tributing to the spot or ring, and θ is the angle of diffraction. Theta (θ) is
determined from the diameter of the idiffraction ring and the sample-to-film
distance. The tangent of 2θ equals the radius of the diffraction ring, r,
divided by the sample-to-film distance, D.

Work Since Last Report

Measurement of Diffraction Patterns

Since we usually do not know either the order, n, or the atomic
spacing, d, for a diffraction ring, the diffraction rings from a particular material
are simply catalogued in terms of d/n, an apparent atomic spacing. Rewriting
the Bragg equation

$$\frac{d}{n} = \frac{\lambda}{2 \sin \theta}$$

But $\quad\quad \tan 2\theta = r/d;$

$$\theta = \frac{\arctan r}{2D}$$

Hence $\quad\quad \dfrac{d}{n} = \dfrac{\lambda}{2 \sin \dfrac{\arctan (r/D)}{2}}$

Since the values of d/n are determined repeatedly for many

diffraction patterns, it is convenient to calculate d/n for the range of r/D

values possible in a particular camera. From an accurate plot, one can then

find d/n very readily.

Table 1 lists the d/n values for diffraction angles (2θ) from 4° to

45°. This table is computed for the average copper $K\alpha$ radiation (1.5418

Angstrom units). Thus, d/n values can be determined readily simply by

measuring the diameters of the diffraction rings on the film. The sample-to-

film distance can be determined by measurement or from the diameter of a

ring produced by an internal standard included with the sample. Magnesium

oxide is a good internal standard. As an internal standard MgO produces a

ring of large diameter which lies outside nearly all rings produced by the

organics. This MgO ring has a d/n value of 2.10, or a r/D value of 0.935.

Hence, the sample-to-film distance, D, equals the radius, r, of this large

MgO ring divided by 0.935.

The diameter of the diffraction rings can be measured directly

from the film. However, we have found this measurement can be accomplished

more readily on the densitometer tracing of the film. Figure 1 is a schematic

diagram of the densitometer. Light from the concentrated filament lamp is

collected by the condensing lens. The lower microscope objective focuses

the region of the condensing lens onto the film emulsion. The glass jaw slit

serves to limit the size of the scanning spot while still providing background illumination for focusing the system. The diffraction rings are usually so broad and diffuse compared to the sharp, narrow line produced by the glass slit, that no benefit comes from using this slit with the powder diffraction patterns. Usually, it is removed for scanning powder patterns. The upper microscope objective focuses the film emulsion on a metal jaw slit before the photo tube. The film is lamped between glass plates to hold it flat and in focus over the entire length of scan. The amount of light reaching the photo tube is reduced by the density or blackening of the particular area of the emulsion interposed between the light source and phototube. The microscope objectives reduce the size of the area scanned to microscopic proportions. Indeed, if the slit is set fine enough, individual slumps or granules of the emulsion are recognized in the output of the phototube. Usually the slit is set wide enough that the granularity of the emulsion does not contribute to the signal. Thus the photo tube current is reduced in proportion to the blackening of the various rings. The blackening is taken as a measure of the intensity of a diffraction ring. The phototube output is recorded on a continuous chart, pen and ink recorder. The diffraction pattern is moved by a lead screw driven by a synchronous motor. The chart paper moves at a much faster rate. Thus, the diameters of the various rings are magnified by ratio of chart travel to film travel per unit time.

Figure 2 is a tracing of the densitometer scan of the diffraction pattern from uric acid. The uric acid pattern is No. 1 of Figure 3. The dark ring of the diffraction pattern produces the peaks at about 7 mm from the center of the scan. A hole is punched in the middle of the film to allow the direct beam of x-rays to bypass the emulsion, preventing blotting out of the central portion of the diffraction pattern. This hole is responsible for the two sharp peaks at the center of the densitometer scan. This pattern does not have a MgO ring. The MgO ring lies outside the scanned area presented here.

Table 2 presents the apparent atomic spacings (d/n) for the compounds which have been catalogued so far. In this table, the d/n values for each compound are listed in the order of decreasing intensity. One of the most striking results presented by this tabulation is the individuality of the patterns. None of the sets of d/n values is repeated for different compounds. Only for the papers is there a correlation in the patterns from the different kinds. This is undoubtedly due to the basic cellulose. The variations in the patterns are probably due to fillers in the papers ro to changes induced in part of the cellulose by the manufacturing process. Note that four d/n values of the dialysis tubing match those from the filter paper. Apparently the cellulose structure is retained even in the transparent product. At the end of table there are several samples identified only by a number. These samples

were submitted by Sam. Sam left us a carbon copy of a list identifying these

samples. None of these numbered samples is a repeat of the other samples

included in Table 2.

Diffraction Patterns from Microgram Samples

For the work reported in Progress Report No. 2 and in Table 2,

the sample was usually contained in a hole 0.5 mm diameter by 0.5 mm long.

This cylindrical hole has a volume of about 10^{-4} cc. Thus, it will hold about

100 micrograms of powdered organic. Pattern No. 1 in Figure 3 was made

from a powdered uric acid sample of about 100 micrograms. This compound

exhibits a very striking diffraction pattern. Note the intense ring about 15 mm

in diameter and the triplet of rings in the center.

No. 2 of Figure 3 is also from uric acid, but here the powdered

sample is contained in a cylindrical hole about 0.1 mm diameter by 0.07 mm

long. This hole has a volume of about 5×10^{-7} cc. Thus this hole would hold

at most about one microgram of uric acid. This small hole is made in lead

foil with a sharp needle. The lead foil is about 0.07 mm thick.

Pattern No. 3 is made from a piece of this lead foil. The streaks

and large spots are characteristic of a large grain, rolled metal. The two

spotty rings from lead foil are visible just outside the uric acid rings in

Pattern No. 2. Hence, the lead rings can serve as an internal standard. The

powdered sample is retained in the hole in the lead foil by a very thin membrane

A very satisfactory pattern has been obtained from one-tenth the amount of uric acid used in making No. 2. The weight of this smaller sample was estimated to be about one-tenth microgram. It was roughly spherical, with a diameter of about 50 microns. A sphere of 50 microns has a volume of 6.5×10^{-8} cc. Thus the weight of a solid sphere of uric acid would be about 1.2×10^{-7} gm.

Discussion

There are problems encountered in obtaining diffraction patterns from the smaller samples. As the sample size becomes smaller, the difficulty in getting the bulk of the sample into the x-ray beam increases. We are now using a collimator of about 80 microns diameter. Thus a 50-micron sample must be carefully centered over the end of the collimator to be bathed by the most intense beam possible. A 500-micron sample need only be positioned so that the edge of the sample hole is not in the x-ray beam. Exposure time is much longer for the smaller sample. Five hours is required to obtain an exposure from the one-tenth microgram sample. An exposure of 15 minutes is sufficient for 100 micrograms. The size of the sample cannot be decreased indefinitely. It may be possible to powder a minute specimen, concentrate the powder in the x-ray beam, and finally obtain an image through long exposure time. However, if there are insufficient crystallite to

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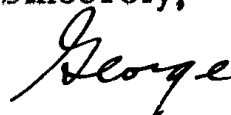
instead of spots, or if the crystallets are too small, then the diffraction pattern

will become unrecognizable.

Further work will consist of perfecting a means for mounting and

positioning microgram specimens, shortening exposure time, and possibly

finding a means of obtaining diffraction patterns from minute single crystals.

Sincerely,

George

Attachments: Figures 1, 2, 3

TABLE 1. APPARENT ATOMIC SPACING*

r/D	d/n	r/D	d/n
0.075	20.612	0.310	5.148
0.080	19.321	0.320	4.999
0.085	18.194	0.330	4.858
0.090	17.181	0.340	4.726
0.095	16.284	0.350	4.601
0.100	15.477	0.360	4.485
0.105	14.746	0.370	4.374
0.110	14.080	0.380	4.269
0.115	13.475	0.390	4.170
0.120	12.915	0.400	4.077
0.125	12.352	0.420	3.904
0.130	11.935	0.440	3.746
0.135	11.502	0.460	3.604
0.140	11.092	0.480	3.474
0.145	10.716	0.500	3.356
0.150	10.366	0.520	3.246
0.155	10.036	0.540	3.146
0.160	9.729	0.560	3.054
0.165	9.438	0.580	2.968
0.170	9.168	0.600	2.888
0.175	8.910	0.620	2.814
0.180	8.670	0.640	2.745
0.185	8.441	0.660	2.681
0.190	8.225	0.680	2.620
0.195	8.007	0.700	2.564
0.200	7.823	0.720	2.511
0.210	7.462	0.740	2.462
0.220	7.134	0.760	2.415
0.230	6.834	0.780	2.371
0.240	6.562	0.800	2.329
0.250	6.309	0.850	2.234
0.260	6.078	0.900	2.152
0.270	5.863	0.950	2.079
0.280	5.666	1.000	2.014
0.290	5.481		
0.300	5.308		

*Apparent atomic spacing (d/n) for values of the

ction angle (2 θ) from
ladiation: Copper Kα - 1.5418 Å.

TABLE 2. TABULATION OF APPARENT ATOMIC PLANE SPACINGS
AND INTENSITY RATIOS FOR THE DIFFRACTION RINGS FROM
SEVERAL POWDERED SAMPLES

The upper row of figures in each case is apparent spacing (d/n). The lower
row of figures is the intensity ratio, I/I_0, taking the most intense ring as I_0.

Na$_2$EDTA Ca	10.33	8.19	17.9	5.77	5.12		
	1.00	0.88	0.87	0.77	0.75		
Na$_2$EDTA Mg	6.28	5.16	4.38	11.56	3.74	3.52	
	1.00	0.69	0.62	0.60	0.60	0.60	
Na$_2$EDTA Zn	6.33	8.98	5.00	12.51	4.30	3.69	3.24
	1.00	0.95	0.90	0.88	0.80	0.75	0.70
Na$_2$EDTA	4.98	3.44	3.10	4.27	7.91		
	1.00	0.96	0.93	0.92	0.83		
Na$_4$EDTA	12.30	7.44	5.53	3.70	4.76	3.28	
	1.00	0.61	0.59	0.53	0.51	0.39	
Hemin	8.98	5.32	4.23	3.71			
	1.00	0.92	0.82	0.75			
50% Hemin)	9.25	13.13	7.14	5.33	4.20	3.65	2.10
50% MgO)	1.00	0.98	0.93	0.89	--	--	--
MgO	4.64	2.10	6.51	2.43	2.32		
	1.00	0.83	0.82	0.45	0.34		
Sulfaguanidine	6.47	4.36	12.60	5.38	3.72	3.13	2.92
	1.00	0.92	0.82	0.78	0.70	--	--
Uric Acid	3.20	3.94	4.89	6.62	5.68	2.93	
	1.00	0.85	0.83	0.80	0.70	0.52	
Carbanthrene Violet	12.23	7.97	3.86				
	1.00	0.99	0.60				
Isopropyl Jade Green	13.88	8.65	4.48	5.94	3.51	3.04	2.53

TABLE 2. TABULATION OF APPARENT ATOMIC PLANE SPACINGS AND INTENSITY RATIOS FOR THE DIFFRACTION RINGS FROM SEVERAL POWDERED SAMPLES (Cont'd)

Sample							
Aspirin	5.58	3.89	11.21	3.29	4.20	2.85	2.53
	1.00	0.72	0.69	0.68	0.67	--	--
8-Hydroxyquinoline	6.18	3.75	3.48	9.27	3.21	4.55	
	1.00	0.89	0.84	0.81	0.81	--	
Dimethylglyoxime	5.72	3.25	5.03	3.59	2.92	2.52	2.31
	1.00	0.86	0.83	0.74	0.35	0.35	0.30
Corn Starch	5.65	7.68	4.94				
	1.00	0.92	0.84				
Paper (20-lb. bond)	3.76	4.02	5.49	3.01	2.48	2.26	6.88
	1.00	0.94	0.80	0.49	0.49	0.45	--
Whatman No. 2 Filter Paper	3.78	4.17	5.50	2.53	3.07	2.27	2.11
	1.00	0.76	0.76	0.45	0.40	--	--
Sulfite Paper	3.87	4.24	5.38	6.61	2.51	2.25	
	1.00	0.85	0.85	0.64	0.50	0.28	
Ethyl Cellulose	10.50	7.95	4.41				
	1.00	0.98	0.79				
Dialysis Tubing	4.19	8.56	3.09	2.52	2.18		
	1.00	0.85	0.48	0.32	0.23		
Formvar	4.74	8.77					
	1.00	0.80					
Mylar	8.41	5.34	3.49	2.68			
	1.00	0.63	0.29	0.21			
Anthracene ($<1\mu g$) on Mylar	4.86	4.08	3.70	3.11	2.73		
	1.00	0.75	0.60	0.46	0.33		
Anthracene	4.50	9.05	3.45	3.01	2.61	2.43	2.29
							--

TABLE 2. TABULATION OF APPARENT ATOMIC PLANE SPACINGS
AND INTENSITY RATIOS FOR THE DIFFRACTION RINGS FROM
SEVERAL POWDERED SAMPLES (Cont'd)

50% Anthracene) 50% MgO)	4.50 1.00	8.92 0.97	4.04 0.54	3.43 0.54	3.00 0.36	2.43 --	2.10 --
Activated Carbon	16.85 1.00	3.69 0.50	2.11 0.10				
Activated Carbon & Crushed Ruby	7.51 1.00	3.41 0.99	2.41 0.64	2.06 0.41	2.35 0.38		
Alumina	5.09 1.00						
NaCl	5.31 1.00	8.93 0.53	3.02 0.49	2.74 0.38			
Ni (foil)	2.02 1.00						
Student Plastilina (Modeling clay)	9.39 1.00						
Paraffin	4.09 1.00	3.66 0.97	16.34 0.78	11.42 0.63	7.92 0.63	2.94 0.22	2.47 0.19
No. 6	5.32 1.00	6.78 0.96	4.27 0.95	4.09 0.86	11.60 0.77	3.79 0.55	3.36 --
No. 7	5.57 1.00	3.68 0.81	7.37 0.74	4.42 0.66	11.10 0.55	2.98 0.30	2.87 0.27
No. 8	3.04 1.00	4.21 0.96	3.38 0.96	4.94 0.92	3.89 0.90	7.80 0.88	6.16 --
No. 9	9.98 1.00	6.80 0.99	4.43 0.97	6.26 0.85	3.86 0.80	3.57 0.50	3.14 0.49
No. 10	4.34 1.00	6.70 0.98	3.68 0.92	5.65 0.83	3.07 0.74	2.78 --	2.63 --
No. 11	8.09 1.00	5.40 0.96	3.96 0.92	4.32 0.91	4.63 0.90	6.68 0.77	3.75 --

TABLE 2. TABULATION OF APPARENT ATOMIC PLANE SPACINGS
AND INTENSITY RATIOS FOR THE DIFFRACTION RINGS FROM
SEVERAL POWDERED SAMPLES (Cont'd)

No. 12	8.25	5.65		
	1.00	0.90		
No. 13	9.10	4.86	2.77	2.59
	1.00	0.92	0.80	0.72
No. 14	8.72	5.61		
	1.00	0.90		
No. 15	8.66	5.34		
	1.00	0.79		

Photo Tube

Recorder

Slit

10-Power
Microscope
Objectives

Material to be Scanned
Sandwiched between
Glass Slides

Glass Jaw Slit

Condensing Lens

Straight Filament Lamp
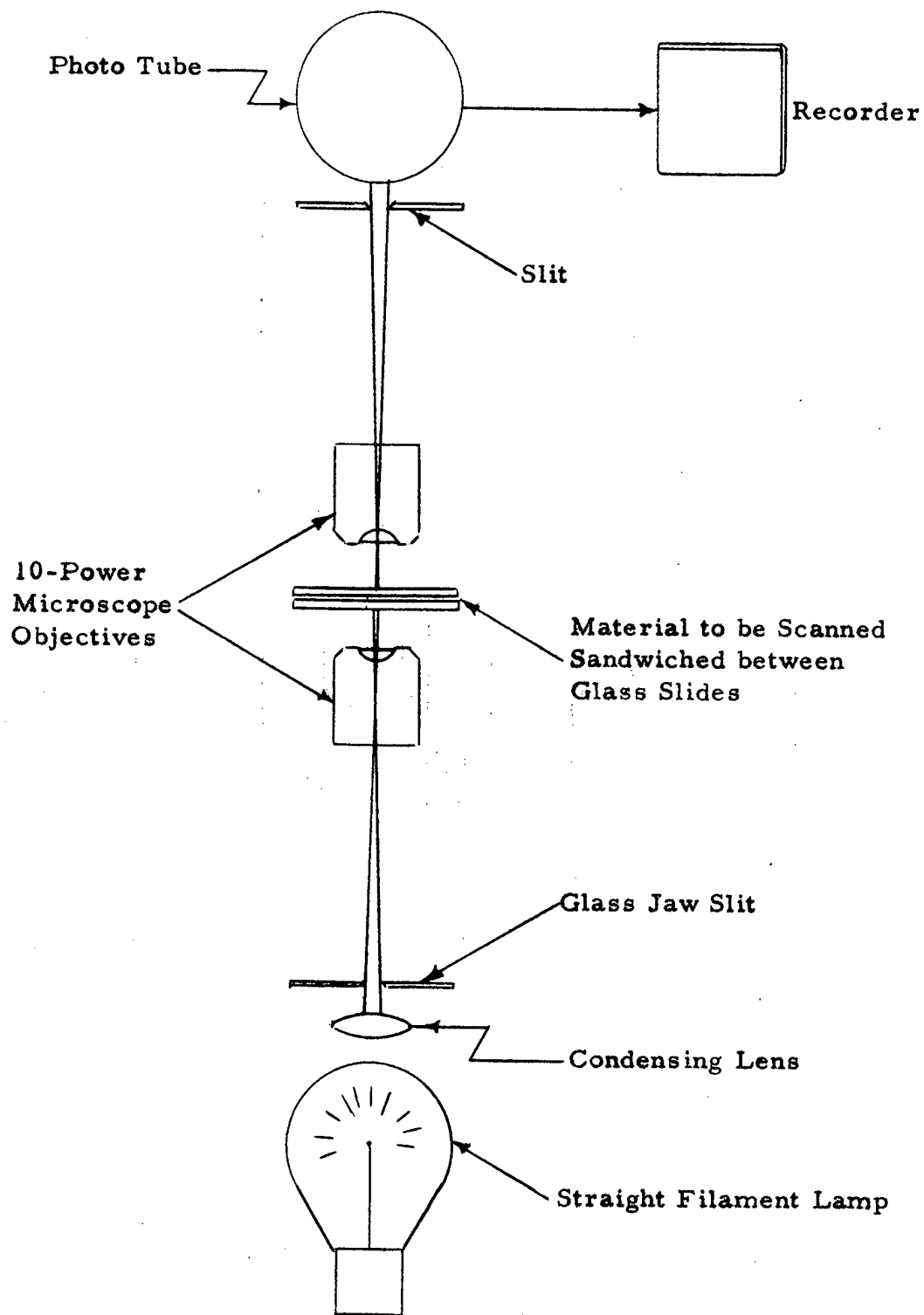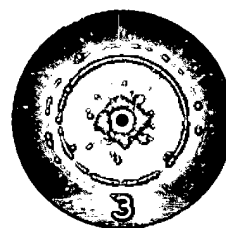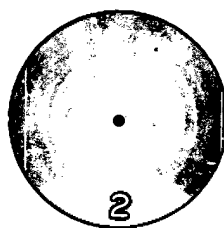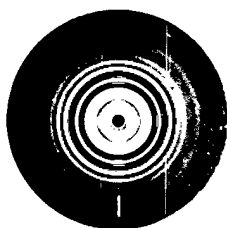
FIGURE 1. DENSITOMETER
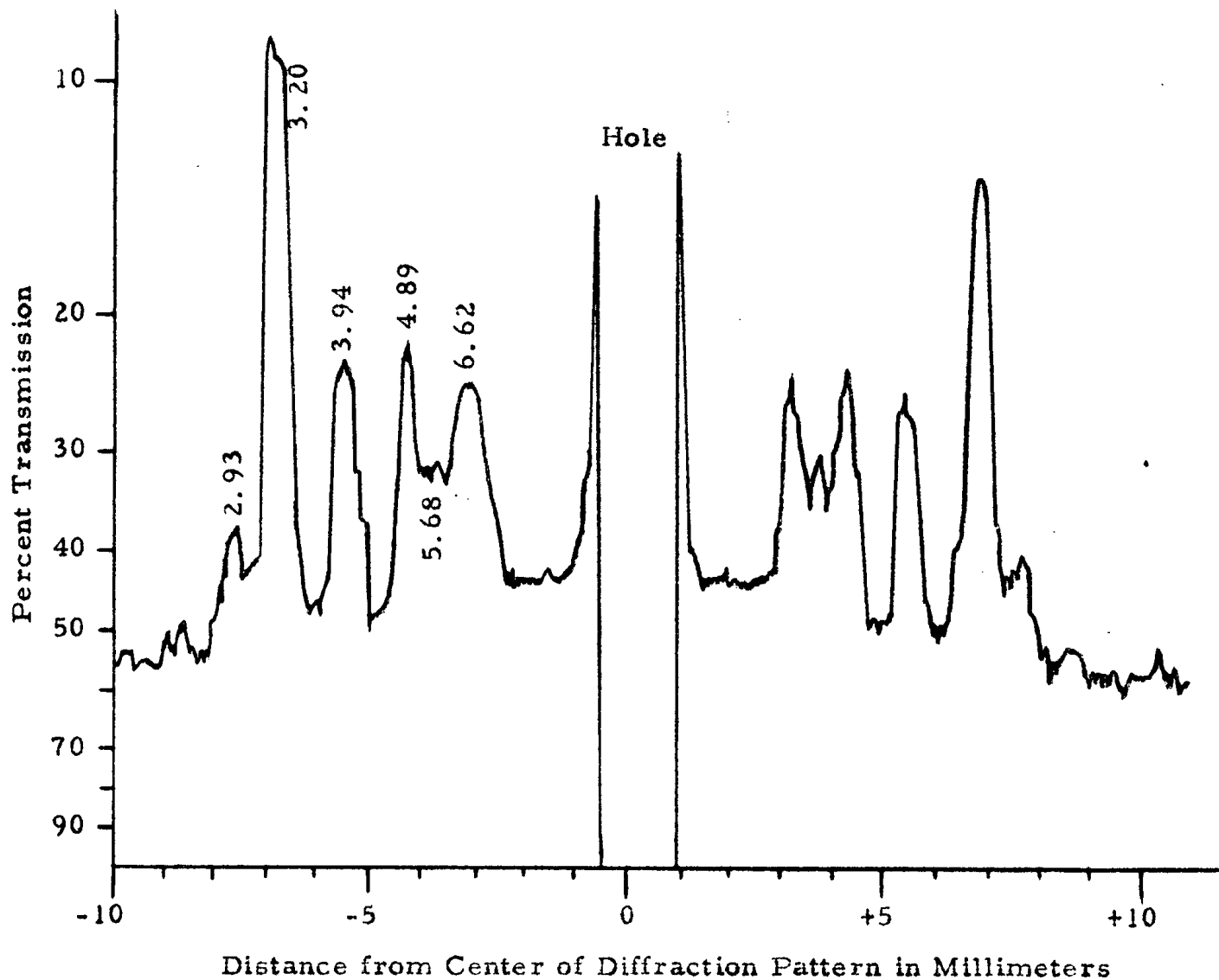
FIGURE 2. REPRESENTATIVE DENSITOMETER SCAN
OF X-RAY DIFFRACTION PATTERN
OF POWDERED URIC ACID
(The numbers by the peaks are the d/n values)

FIGURE 3. X-RAY DIFFRACTION PATTERNS

1.   Uric acid (about 100 micrograms).

2.   Uric acid (about one microgram).

3.   Lead foil (about 3/1000-inch thick).

γ-ray

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